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ORGANIC CHEMISTRY

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WORTH PUBLISHERS, INC.

To Our Parents and to Cathy

Organic Chemistry

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		1s	2s	2p
Helium	$1s^2$	$\uparrow\downarrow$		
Lithium	$1s^2 2s^1$	$\uparrow\downarrow$	\uparrow	
Beryllium	$1s^2 2s^2$	$\uparrow\downarrow$	$\uparrow\downarrow$	
Boron	$1s^2 2s^2 2p^1$	$\uparrow\downarrow$	$\uparrow\downarrow$	\uparrow
Carbon	$1s^2 2s^2 2p^2$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\uparrow$
Nitrogen	$1s^2 2s^2 2p^3$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\uparrow\uparrow$
Oxygen	$1s^2 2s^2 2p^4$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow\uparrow$
Fluorine	$1s^2 2s^2 2p^5$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow\uparrow\downarrow$

Figure 1-4

Electronic configurations of first- and second-row elements.

1.14 The Molecular Orbitals of the Hydrogen Molecule

The hydrogen molecule provides a starting point for examining the molecular-orbital model for chemical bonding. If two hydrogen atoms are allowed to approach each other, the two hydrogen $1s$ atomic orbitals interact to form two molecular orbitals. One of these is a bonding orbital, which is more stable than the atomic orbitals from which it is formed; the other is an antibonding orbital, which is less stable than the $1s$ atomic orbitals.

In order for a bonding molecular orbital to be more stable than the atomic orbitals from which it is formed, the atomic orbitals must overlap. We can represent overlap, which is a mathematical concept, by the simple pictures of Figure 1-5. Two orbitals overlap only if a part of each orbital occupies the same region of space. The degree of overlap provides a simple measure of the increase in stability of the bonding molecular orbital that is formed.

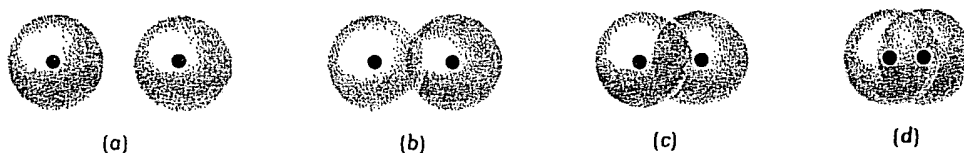


Figure 1-5

Formation of bonding molecular orbitals by interaction of two hydrogen

$1s$ atomic orbitals. Orbital overlap increases in the order (a) to (d).

The extent of overlap indicates the degree of molecular stabilization resulting from the attraction between oppositely charged nuclei and electrons. If overlap alone determined the stability of a bond, the most stable molecule would be formed with overlap at a maximum, i.e., when the two nuclei coincide. However, repulsion of the like-charged nuclei increases as the nuclei are brought together. The most stable molecular orbital results when the two nuclei are separated by a distance that allows a substantial amount

of orbital overlap without too great a nuclear repulsion. For the hydrogen molecule, the most stable molecular orbital results from a nuclear separation of 0.074 nm, which is the bond distance observed experimentally [1 nm = 1 nanometer = 10^{-9} m = 10 angstrom units (\AA)].

The hydrogen molecule is thus described as consisting of two electrons of opposing spin, each contained in the bonding molecular orbital formed from the overlap of two hydrogen 1s atomic orbitals (Figure 1.6).

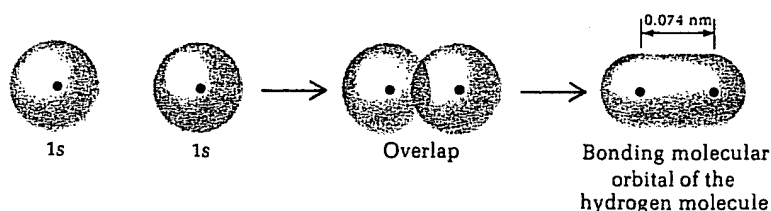


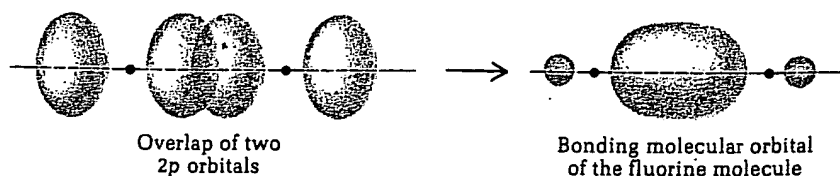
Figure 1-6
Formation of the bonding molecular orbital of the hydrogen molecule by the overlap of two hydrogen 1s orbitals.

1.15 The Bonding Orbital of the Fluorine Molecule; Sigma Bonds

We have seen that two atomic orbitals of hydrogen combine to form two molecular orbitals. The bonding orbital, which is the more stable, contains the electron pair of the single bond of the hydrogen molecule. In general, we shall find that molecular orbitals are formed from two or more of the atomic orbitals that belong to different atoms of a molecule. From n atomic orbitals that can overlap we can expect n molecular orbitals. Roughly half of these are bonding molecular orbitals, which are more stable than the average of the atomic orbitals from which they are formed. An equal number are antibonding orbitals, which are less stable than the average of the atomic orbitals. Some properties of antibonding orbitals are discussed in Chapter 30.

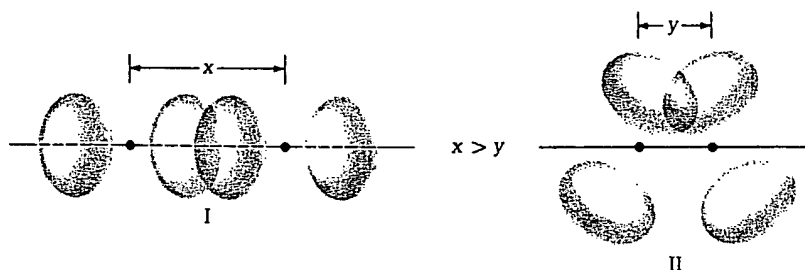
As a second example of the formation of a molecular orbital, let us consider the fluorine molecule, F_2 . The molecular orbitals of F_2 must be formed by overlap of atomic orbitals of a pair of fluorine atoms. Recalling that a fluorine atom has filled 1s and 2s orbitals and that its three 2p orbitals contain five electrons (Figure 1.4), we see that a 2p orbital with only one electron is available for bond formation. Let us consider the molecular orbital that can be formed by the overlap of two 2p orbitals from a pair of fluorine atoms.

End-to-end overlap between these orbitals generates a bonding molecular orbital in which the overlap region lies between the fluorine nuclei. The assignment of the two electrons of the two 2p orbitals to the bonding molecular orbital allows these electrons to be stabilized by the attraction of the two nuclei:



hydrogen
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y [1 nm =
o electrons
tal formed

The bonding molecular orbital of the fluorine molecule lies symmetrically about the line joining the nuclei. It must have this form because of the trade-off between orbital overlap and nuclear repulsion. We can see why if we consider an alternative orbital overlap that does not occur end to end, as in II. The overlap of I and II is similar, but the nuclei achieve a greater separation in I. Greater nuclear repulsion makes II less stable than I:

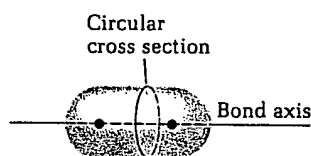


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Bonds formed by the end-to-end overlap of atomic orbitals are called sigma bonds, symbolized by the Greek letter σ .† The characteristic feature of a sigma bond is the symmetry of its electron density. Imagine that the bond is cut by a perpendicular plane; the resulting cross section of the electron density is a circle, centered about the bond:



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2 must be
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2p orbitals
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of fluorine

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Problem 1-10 Construct a molecular-orbital picture of the bonding in the HF molecule. What atomic orbitals are used?

1-16 Hybrid Orbitals

The bonds formed by carbon and by most other elements of the second row of the periodic table are usually formed not by overlap of pure 2s or 2p atomic orbitals but by overlap of hybrid atomic orbitals that are partly s and partly p. Hybrid orbitals have better overlap properties than pure s or p orbitals, and they allow an atom to form a maximum number of bonds spaced as far apart as possible.

The three types of hybrid orbitals formed by second-row elements are termed sp , sp^2 , and sp^3 . Let us examine how each type arises. As we have seen, the valence shell of a second-row atom consists of one 2s and three 2p atomic orbitals. When all four of these are combined, four sp^3 hybrid atomic orbitals are formed. Each one is oriented toward a corner of a tetrahedron, and each consists of a small lobe near the nucleus and a large lobe extending some distance from the nucleus (Figure 1-7).

† The Greek alphabet is listed in Appendix A.

ur orbital
olecule

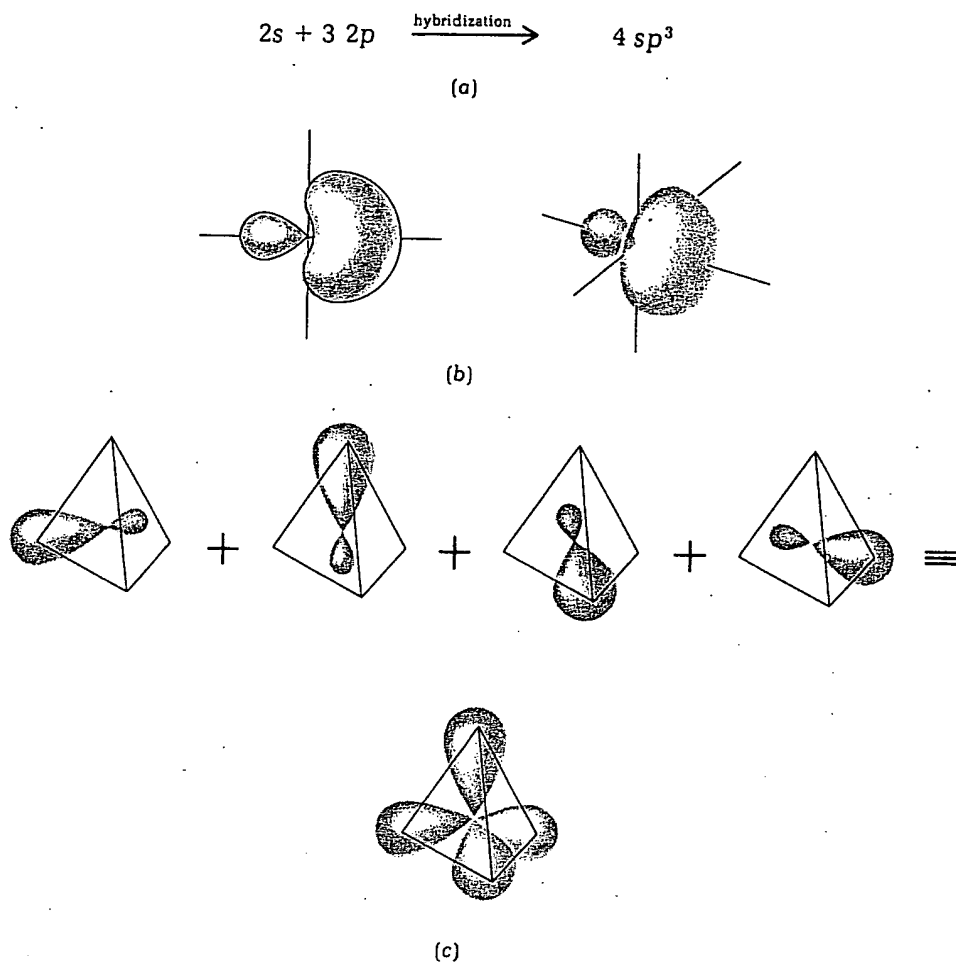


Figure 1-7

(a) Combination to form four sp^3 hybrid atomic orbitals; (b) contour diagram of one sp^3 hybrid atomic

orbital; and (c) tetrahedral geometry of the four sp^3 hybrid orbitals.

The superscript numerals used in designating the hybrid orbital identify the number of each of the types of pure atomic orbitals that combine to form the hybrid: sp^3 means a hybrid of one s and three p orbitals. In any hybridization process the number of pure orbitals combined always equals the number of hybrid orbitals formed: a total of four orbitals combine to form four sp^3 hybrid orbitals.

Suppose that only two $2p$ atomic orbitals are allowed to form hybrids with the $2s$ atomic orbital. Three sp^2 hybrid atomic orbitals result. Each is oriented toward the corner of an equilateral triangle and resembles the sp^3 orbital in contour, except that the two lobes are more nearly equal in shape and the larger lobe does not extend as far from the nucleus (Figure 1-8). Formation of the three sp^2 hybrid orbitals leaves one $2p$ orbital unchanged. This $2p$ orbital is oriented perpendicularly to the plane of the three hybrid orbitals (Figure 1-8d).

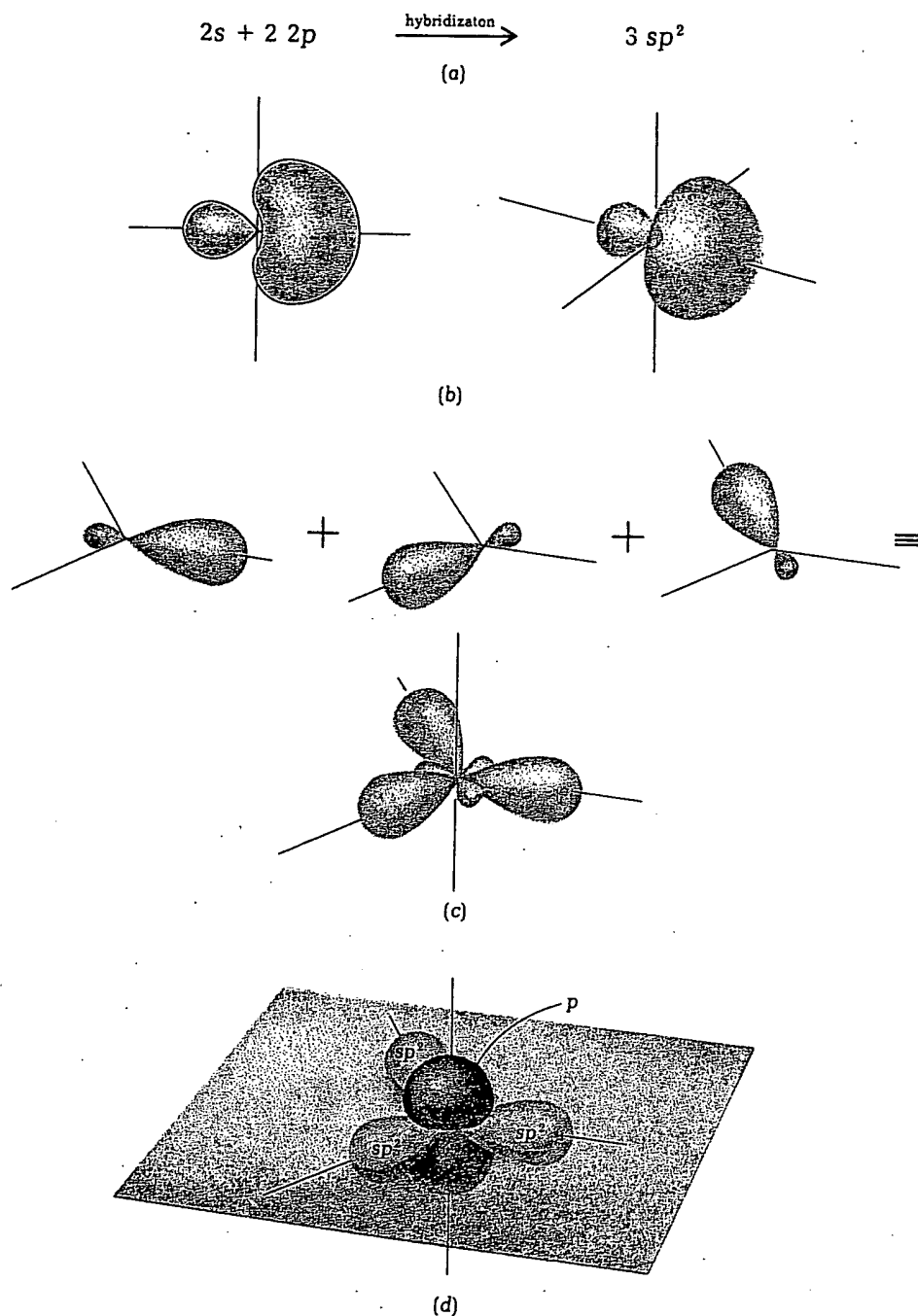


Figure 1-8
 (a) Combination to form three sp^2 hybrid atomic orbitals; (b) contour diagram of one sp^2 hybrid atomic orbital; (c) trigonal geometry of three sp^2 hybrid atomic orbitals; and (d) the orientation of the three sp^2 hybrid atomic orbitals and the remaining p orbital.

Finally, combination of the $2s$ atomic orbital with one of the $2p$ orbitals generates two sp hybrid orbitals. Each orbital is oriented along a line, and the major lobes of the two hybrids point in opposite directions along the line (Figure 1-9). Formation of the two sp hybrid orbitals leaves two $2p$ orbitals unchanged. They are oriented perpendicularly to each other and to the axis of the hybrid orbitals (Figure 1-9d).

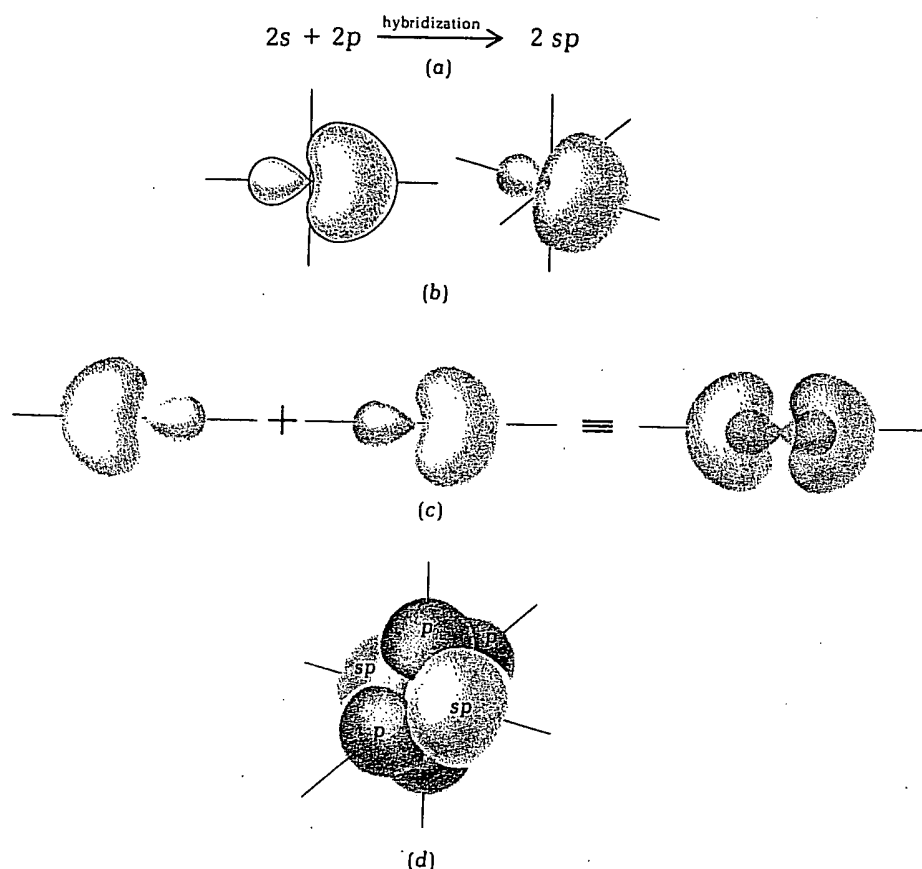


Figure 1-9

(a) Combination to form sp hybrid orbitals; (b) contour diagram of the sp hybrid atomic orbital; (c) linear orientation of the two sp hybrid atomic

orbitals; and (d) the orientation of the two sp hybrid atomic orbitals and the remaining two p orbitals.

1.17 Molecular Orbitals for Methane and Ethane; Molecules with sp^3 Hybridization at Carbon

Now let us consider the formation of molecular orbitals from hybrid atomic orbitals. The molecule methane, CH_4 , is known from physical measurements to have a tetrahedral arrangement of hydrogen atoms. Consequently, we must

use tetrahedrally oriented sp^3 hybrid orbitals in describing the bonding at carbon. Each of the four sp^3 orbitals of carbon can overlap with a $1s$ orbital of hydrogen to form an sp^3 - s bonding molecular orbital, which can accommodate one electron pair (Figure 1-10a).

Recalling that carbon has a total of four electrons in its valence shell and each hydrogen atom has one valence electron, we see that the atoms of the methane molecule have a total of eight valence electrons. They are assigned in pairs, two electrons with opposite spins, to each of the four sp^3 - s bonding molecular orbitals. From the symmetry of the electron density in these orbitals we see that the methane molecule is held together by four σ bonds (Figure 1-10b). The tetrahedral geometry of the methane molecule orients the electrons in the four bonds as far apart as possible. This separation of like-charged electrons contributes to the stability of any carbon atom bonded to four atoms or groups by sp^3 hybrid orbitals.

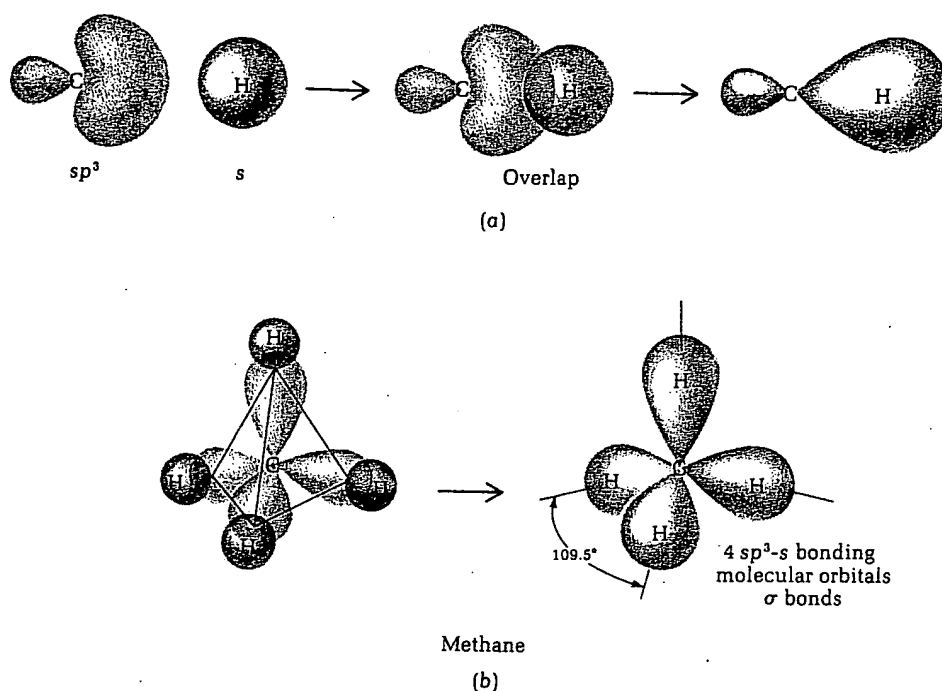


Figure 1-10
Molecular orbitals of methane: (a) a single sp^3 - s bonding molecular orbital for a C—H σ bond of methane; (b) four sp^3 - s bonding molecular orbitals, σ bonds.

This analysis has followed a useful stepwise procedure: (1) the geometry of the molecule is used to assign a hybridization to each second-row atom; (2) the hybrid atomic orbitals are visualized as combining to form bonding molecular orbitals; and (3) the valence electrons of the molecule are assigned in pairs to the molecular orbitals. We can apply these steps to develop the molecular-orbital model for ethane, C_2H_6 . As with the methane molecule, the

bonds of ethane are known to assume a tetrahedral geometry, and the carbon atoms must be assigned an sp^3 hybridization. The carbon-carbon single bond of ethane must be described as a bonding molecular orbital formed by the overlap of two sp^3 hybrid atomic orbitals, one from each carbon atom. The remaining three sp^3 atomic orbitals of carbon overlap with $1s$ orbitals of hydrogen, forming a total of six sp^3-s bonding molecular orbitals. The resulting seven bonding atomic orbitals are filled by the fourteen valence electrons of two carbon atoms and six hydrogen atoms. The ethane molecule is made up of seven σ bonds; it can be regarded as two tetrahedral carbon units linked at one vertex (Figure 1.11).

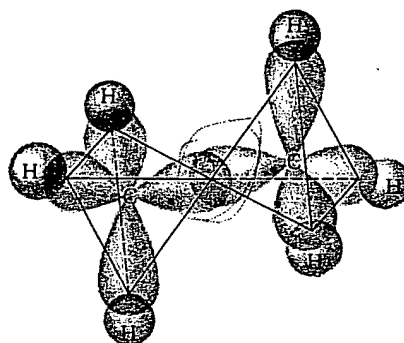


Figure 1.11
Molecular-orbital picture of ethane.

1.18 Molecular Orbitals for Ethylene; A Molecule with sp^2 Hybridization at Carbon

From physical measurements, ethylene, C_2H_4 , is known to be a planar molecule in which each carbon atom assumes a trigonal geometry. We can therefore conclude that the molecular-orbital representation of ethylene must assign an sp^2 hybridization to each of its carbon atoms. Let us see how the representation can be developed from this conclusion.

The overlap of two sp^2 atomic orbitals, one from each carbon atom, results in the formation of an sp^2-sp^2 bonding molecular orbital. The remaining four sp^2 atomic orbitals overlap with $1s$ atomic orbitals of hydrogen atoms, forming four sp^2-s bonding molecular orbitals. The resulting five bonding molecular orbitals can be filled by 10 of the 12 valence electrons contributed by the four hydrogen and two carbon atoms of ethylene. The result is five σ bonds belonging to ethylene (Figure 1.12a). The remaining two electrons of the ethylene molecule are assigned to a new type of bond, a π bond, which results from the overlap of the two p orbitals belonging to the carbon atoms. These p orbitals are not directed toward each other; their axes are parallel. Overlap of a new kind can occur between the two top lobes and the two bottom lobes of these p orbitals, forming a bonding molecular orbital with electron density above and below the plane of the carbon atoms but no electron density on that plane. The bond resulting from this type of edgewise overlap of parallel p orbitals is called a π bond (Figure 1.12b). From the figure we can see that in molecular-orbital terms the carbon-carbon double bond consists of an sp^2-sp^2 σ bond and a $p-p$ π bond.

the carbon
single bond
formed by the
carbon atom. The
orbitals of
the carbon atom
are made up
of units linked

of ethane.

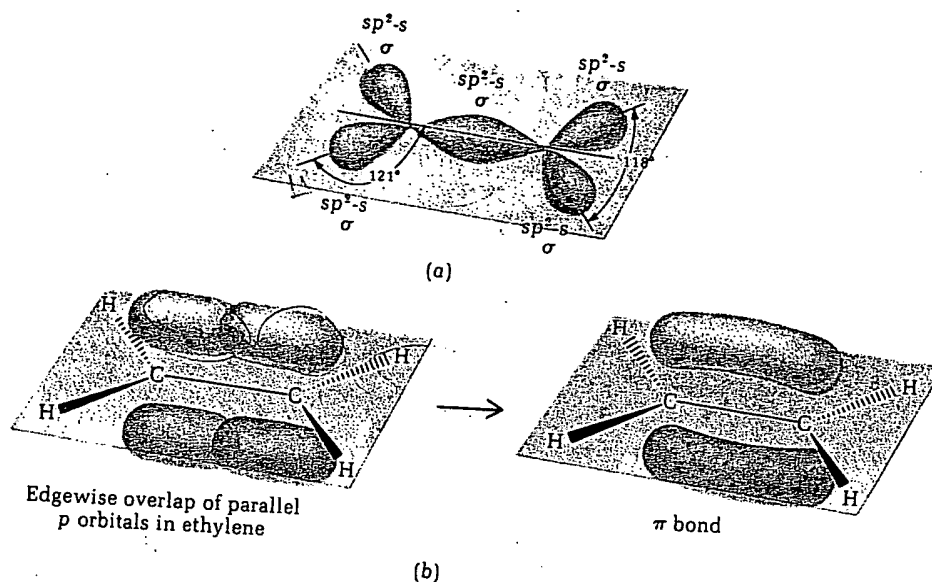


Figure 1-12
Molecular-orbital picture of ethylene:
(a) σ bonds of ethylene and (b) π bond
of ethylene. A solid wedge-shaped line
is used for a bond that is coming out

of the plane of the paper toward the
reader. A series of short parallel lines
is used for a bond that is pointing into
the paper away from the reader.†

Problem 1-11 Acetylene, $\text{H}-\text{C}\equiv\text{C}-\text{H}$, is a linear molecule. What hybridization is assigned to its carbon atoms? Draw a molecular-orbital picture of the σ bonds and π bonds of acetylene.

1.19 Bond Angles and Hybridization of Methane, Water, and Ammonia

The angle between two bonds at an atom is called a **bond angle**. For molecules like methane that have a tetrahedral geometry, all bond angles are 109.5° , the tetrahedral angle. We can expect to find this angle at any atom that assumes an sp^3 hybridization.

The bond angle of ammonia is 107.3° , and the angle of water is 104.5° . These values are close to the tetrahedral value, and it is believed that the N—H and O—H bonds of ammonia and water are formed by overlap of hydrogen 1s orbitals with orbitals of nitrogen and oxygen that have slightly more p character than a pure sp^3 hybrid. The lone-pair electrons of water or ammonia are assigned to hybrid orbitals that are sp^3 hybrids with a slight excess of s character. Viewing the lone pairs as part of the water and ammonia structures, we see that each is tetrahedral with a slightly distorted geometry (Figure 1-13).

We shall find many structures in which neutral carbon atoms are bonded to four atoms or groups, neutral nitrogen atoms are bonded to three atoms or groups, and neutral oxygen atoms are bonded to two atoms or groups.

† For an explanation of graphical signs and symbols used in the text see Appendix C.

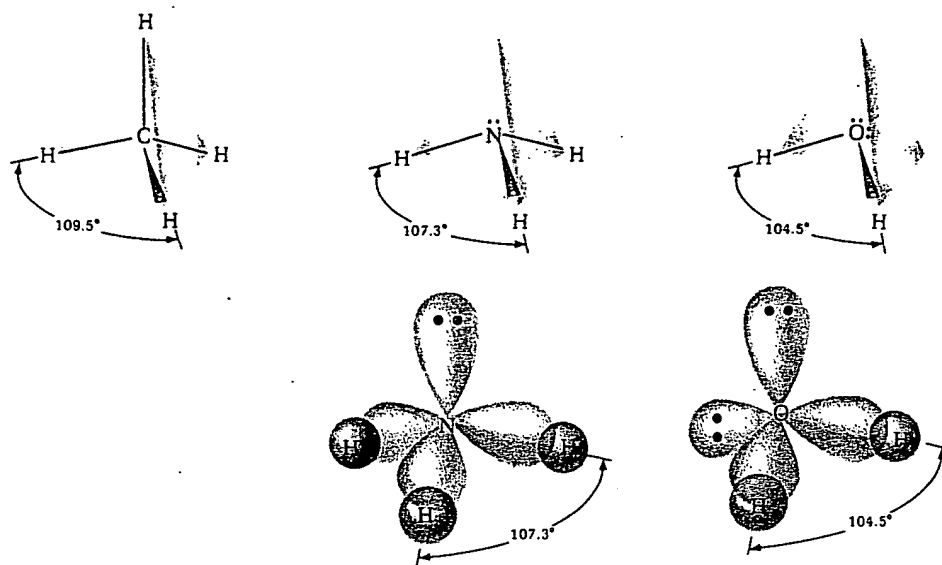


Figure 1-13
Depictions of the tetrahedral geometry
of the methane, ammonia, and water
molecules.

From many physical measurements on different molecules, it is clear that their carbon, nitrogen, and oxygen atoms have bond angles close to the tetrahedral value. These atoms can be assigned a hybridization close to sp^3 .

Like bond angles, bond distances tend to assume values that are nearly constant for a given pair of bonded atoms. Some representative values of bond distances are shown in Table 1-1. We have seen that a chemical bond has a fixed length determined by a trade-off between orbital overlap and nuclear repulsion. For elements below the second row of the periodic table the atomic orbitals extend farther from the nucleus than the orbitals of the second-row element in the same column. As a result, these elements form unusually long bonds. We can see an example of this effect by comparing the bond lengths of HF, HBr, and HI.

Table 1-1 Average Bond Distances

Bond	Length, nm†	Bond	Length, nm†
$\begin{array}{c} \\ -C-H \\ \end{array}$	0.109	$\begin{array}{c} H-O \\ \end{array}$	0.096
$\begin{array}{c} & \\ -C & -C- \\ & \end{array}$	0.154	$\begin{array}{c} H-F \\ \end{array}$	0.092
$\begin{array}{c} >C=C< \end{array}$	0.133	$\begin{array}{c} H-N- \\ \end{array}$	0.101
$-C\equiv C-$	0.120	$H-Br$	0.142
		$H-I$	0.161

† 1 nm = 10^{-9} m.

1-20 Free and Hindered Rotation about Single and Double Bonds; Isomers

By relying on the molecular-orbital model we can explain two important facts about single bonds and double bonds. Two groups that are linked by a single bond are free to rotate about that bond; groups that are linked by a carbon-carbon double bond are not. Let us first consider the rotation of groups about the single bond.

Ethane, $\text{CH}_3\text{—CH}_3$, which consists of two —CH_3 groups linked by a single bond, can be represented by any of a series of structures that differ only in the relative positions of the hydrogen atoms of the two —CH_3 groups. Structures like these that can be interconverted by a rotation about a single bond are called conformations. The staggered conformation (Figure 1-14a) is the most stable conformation of ethane, and 99 percent of the molecules in a sample of ethane have this structure. Alternative conformations that are less stable are called the skew and eclipsed conformations (Figure 1-14b and c).

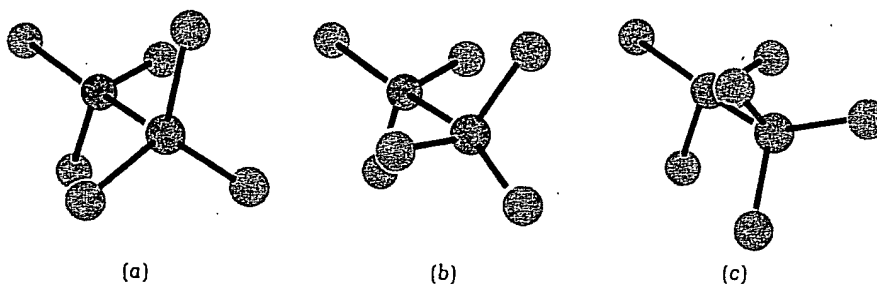




Figure 1-14
Conformations of ethane: (a) staggered, (b) skew (one of an infinite number of examples), and (c) eclipsed.

If we could examine the molecules in a sample of ethane at room temperature, we would find that staggered ethane molecules rapidly undergo bond rotation and conversion into skew or eclipsed ethane molecules, which in turn rapidly reconvert into the staggered conformation. This process repeats itself continually with all molecules in the sample. Although to be strictly accurate we must speak of ethane molecules as capable of assuming all three conformations, for many purposes we can assign the most stable (staggered) conformation as the structure of ethane. We pursue the important topic of conformation in Chapter 13.

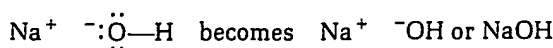
How can we use the molecular-orbital scheme to explain the existence of different conformations of ethane? We can answer this question by noting that the C—C bond is a σ bond, for which orbital overlap cannot depend on the orientation of the groups attached by the bond. For this reason, the stabilities of the three ethane conformations are expected to be the same, and rotation about the C—C bond is expected to be very ready. As we have seen, the staggered conformation is found experimentally to be slightly more stable than the eclipsed or skew conformations. This small energy difference cannot be explained by a simple molecular-orbital picture, although more refined orbital models have been proposed that do so.



cis-1,2-Dichloroethylene,
molecular formula $C_2H_2Cl_2$,
bp $60.3^\circ C$

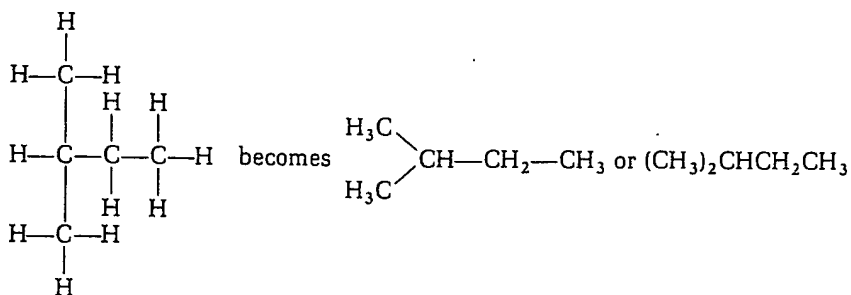
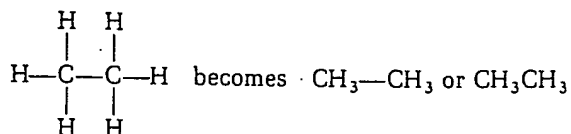
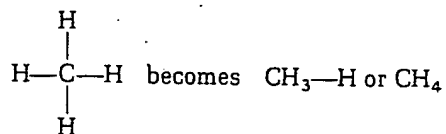


trans-1,2-Dichloroethylene,
molecular formula $C_2H_2Cl_2$,
bp $47.7^\circ C$

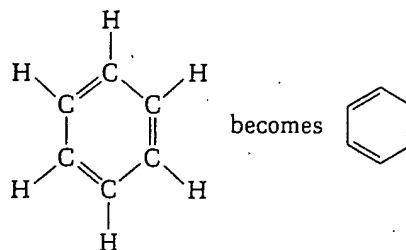
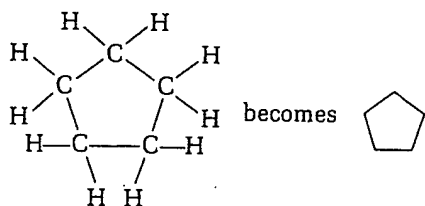
$$\begin{array}{ccccccc} \text{H}-\ddot{\text{O}}-\text{H} & \text{becomes} & \text{H}-\text{O}-\text{H} & & \text{H}-\ddot{\text{N}}-\text{H} & \text{becomes} & \text{H}-\text{N}-\text{H} \\ & & & & | & & | \\ & & & & \text{H} & & \text{H} \end{array}$$


2. A common abbreviation consolidates C—H bonds to form part structures, using —CH₃ (methyl), —CH₂— (methylene), or —CH— (methine)

for tetrahedral carbon bonded to three, two, or one hydrogen atom, respectively:



3. Another abbreviation is frequently applied to structures that contain rings. The ring structure is simplified by omitting the symbol C for a carbon atom and by omitting hydrogen atoms:



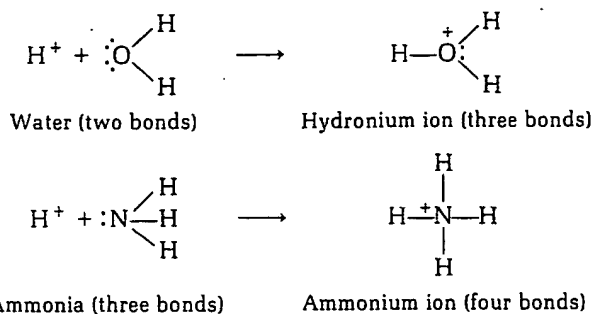
Structures with no atoms specified at the intersections of bonds are assumed to have carbon atoms at the intersections. Structures lacking sufficient atoms or bonds to satisfy the rules of valence are assumed to have enough hydrogen atoms bonded at each valence-deficient site to give each carbon atom a filled valence shell.

Reactions of Acids and Bases

1.22 Lewis Acids and Bases

The free proton, H^+ , is not a species that can be prepared in the organic laboratory, although it can be generated in the near vacuum of a mass spectrometer (Chapter 12) by bombardment of hydrogen molecules with high-energy electrons. Once formed, the proton is found to react upon collision with molecules bearing lone pairs. For example, with water the free proton

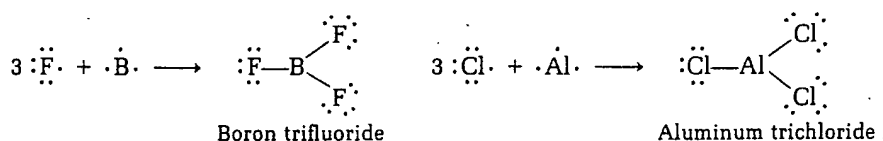
reacts to form the hydronium ion, and with ammonia it reacts to form the ammonium ion:



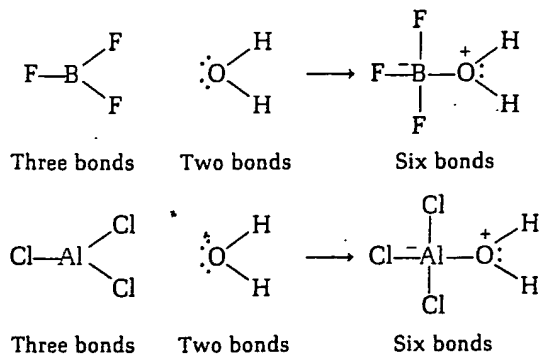
The free proton or hydrogen ion is the simplest example of a Lewis acid; ammonia and water are common Lewis bases. A Lewis acid is a substance that can act as an electron-pair acceptor. A Lewis base is a substance that can react with a Lewis acid as an electron-pair donor. Several important and general features of the reactions of Lewis acids and bases can be learned from the two proton reactions above.

We first note that the proton does not have a filled valence shell but is electron-deficient. Electron deficiency allows the proton to serve as an electron-pair acceptor, or Lewis acid. We next note that in both reactions a new bond is formed by sharing the electrons of a lone pair with the electron-deficient proton. The positive charge of the free proton becomes a formal positive charge on the oxygen or nitrogen atoms of the products.

We now examine some Lewis acids of more complex structure, those formed by boron or aluminum. These elements have only three valence electrons and can form only three bonds by electron sharing with atoms such as fluorine or chlorine. Three bonds allow boron or aluminum only six shared electrons, two short of eight:



Because they bear only six valence electrons, the boron of boron trifluoride and the aluminum of aluminum trichloride can act as electron-pair acceptors, and these molecules are therefore Lewis acids. Let us examine their reactions with the Lewis base water:



Comparing the structures of starting materials and products, we first notice that all the bonds in the starting materials also appear in the products but each product has an additional bond. It results from sharing the lone pair of the Lewis base, water, with the electron-deficient boron or aluminum atom of the Lewis acid. Note also that both starting materials are neutral but the formation of the new bond results in a formal negative charge on boron or aluminum and a formal positive charge on oxygen. The boron or aluminum atoms of the products are assigned eight valence electrons, unlike the corresponding atoms of the starting materials.

We have now seen four examples of reactions of Lewis acids with Lewis bases. In each of these reactions the driving force can be regarded as the tendency of the electron-deficient atom of the Lewis acid to complete its valence shell by sharing the electron pair of the Lewis base. Equivalently, we can observe that the product of a Lewis acid-base reaction always contains one more bond than the starting materials. This additional bond tends to stabilize the product. The chapters that follow contain many examples of the Lewis acid-base reactions of carbon derivatives.

Common examples of Lewis bases include many anions, as well as neutral derivatives of oxygen and nitrogen:

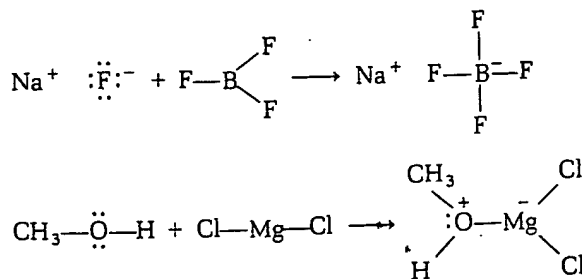
Examples of Lewis bases: H_2O , NH_3 , NaOH , NaF , NaCN , CH_3NH_2 , CH_3OH , CH_3OCH_3

Common examples of Lewis acids include trivalent derivatives of boron and aluminum, as well as salts of many metals:

Examples of Lewis acids: BF_3 , BX_3 , AlCl_3 , AlX_3 , FeCl_3 , SnCl_4 , ZnCl_2 , LiCl , MgCl_2 , where X = many atoms or groups

The following three-step procedure can be used to write the structure of the complex formed by the reaction of any Lewis acid with a Lewis base:

1. Identify the electron-deficient atom of the Lewis acid and the atom of the Lewis base that bears the basic lone pair.
2. Redraw the structures of the acid and the base, leaving all bonds intact but adding a new bond between the electron-deficient atom and the lone-pair-bearing atom identified in step 1.†
3. Assign correct formal charges to the atoms of the complex. For example,



† Lone pairs are often omitted from atoms, particularly F or Cl, that are not involved in bonding changes.

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